metallacyclopentadiene of the type in *d* from the decomposition of thiophene on Pt(111). Steps 1, 2, and 3 constitute a new mechanism for the cleavage of both C–S bonds prior to any hydrogenation of the thiophene ring. Although other mechanisms for thiophene HDS involving C–S cleavage prior to hydrogenation have been proposed,[31] none is based on reactions which are known to occur on metal centers.

Following the formation of intermediate *d* in Scheme IV, the C_4 ring and sulfide could be removed from the catalyst by reaction with adsorbed hydrogen to give butadiene and H_2S. The mechanism in Scheme IV shows the adsorbed hydrogen in the form of surface hydrides M–H; however, it is also possible that the hydrogen is present in –SH groups; there is ample evidence to suggest that –SH ligands may be a good source of hydrogen atoms.[32] To our knowledge, there are no examples of H_2S elimination from M(H)(SH) or $M(H)_2(S)$ complexes which would support step 5; however, there are several reports of the reverse reaction, i.e., H_2S addition to mononuclear[33] or polynuclear[34] metal complexes to give products with H, SH, or S ligands. Thus, the mechanism in Scheme IV represents a reasonable process for thiophene desulfurization.

Unlike our previous mechanism (Scheme I), that in Scheme IV does not involve initial hydrogenation of the thiophene ring and therefore, represents a fundamentally different type of thiophene HDS mechanism. Results of reactor studies have been interpreted[32] to suggest that there are two HDS processes occurring at different sites; one begins by initial hydrogenation of thiophene while the other begins with C–S bond cleavage. Schemes I and IV represent reasonable mechanisms for these processes; both are based on known reactivity of thiophene in its organometallic complexes. It remains to be determined whether or not similar processes occur on HDS catalyst surfaces.

Acknowledgment. We appreciate the loan of $IrCl_3$ from Johnson Matthey, Inc.

Supplementary Material Available: Tables of positional parameters, additional bond angles, torsion angles, displacement parameters, and least-squares planes for complexes **3**, **7**, **8**, and **9** (39 pages); listing of calculated and observed structure factors (55 pages). Ordering information is given on any current masthead page.

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Stable Polyradicals with High-Spin Ground States. 1. Synthesis, Separation, and Magnetic Characterization of the Stereoisomers of 2,4,5,6-Tetrachloro-$\alpha,\alpha,\alpha',\alpha'$-tetrakis(pentachlorophenyl)-*m*-xylylene Biradical[1]

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Abstract: Biradical **3** and its corresponding monoradical **6** have been synthesized and isolated as stable solids at ambient conditions. Biradical **3** exists in three stereoisomeric forms due to restricted correlated rotation of the aryl groups. It has been obtained as a 60:40 equilibrated mixture of the *meso* form (C_s symmetry) and the enantiomeric *dl* pair (C_2 symmetry) which have been unambiguously identified by ESR spectroscopy. Recrystallization of the diastereoisomeric mixture afforded the pure *meso* form. Both diastereoisomers have been separated by HPLC chromatography and their interconversion rates have been measured at different temperatures. The diastereoisomerization barrier [$\Delta G^{\ddagger}_{298K}$ (*meso* → *d*(or *l*)) = 98 kJ mol^{-1}] is comparable to that of related monoradicals with similar steric hindrances. Intense triplet ESR signals were obtained in rigid media, being $|D/hc| = 0.0152$ and $|E/hc| = 0.0051$ cm^{-1} for the *meso* and $|D/hc| = 0.0085$ and $|E/hc| \leq 0.003$ cm^{-1} for the *dl* isomer. The observed zero-field splitting parameters for both stereoisomers are consistent with their symmetries. Curie plot studies on ESR signals are in agreement with triplet ground states for both diastereoisomers irrespective of their symmetries. Magnetic susceptibility and magnetization measurements of the diastereoisomers in solid state show quasi-ideal $S = 1$ paramagnetic behavior down to 4.2 K. For one representative case, the results presented here validate the current theories for the prediction of ground-state multiplicities in nondisjoint AH, regardless of the lack of planarity and changes in the symmetries.

Current research on magnetic organic materials aims toward the design and preparation of organic ferromagnets. Although no such substance has been so far found, several strategies and theoretical models have been described for designing this type of material.[2] One of these strategies consists of obtaining molecules possessing a spin multiplicity as high as possible and having them

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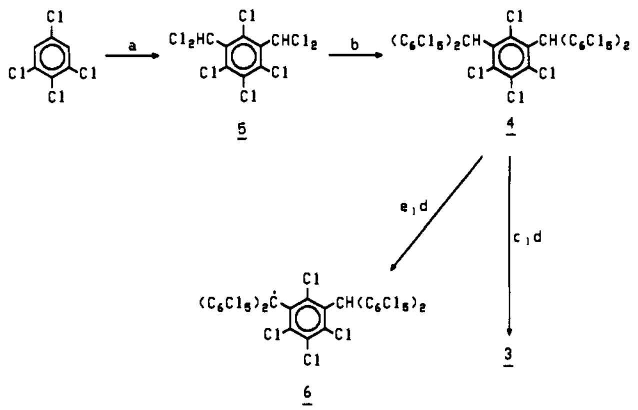
[1] A brief report of this work was presented at the Symposium on Ferromagnetic and High-Spin Molecular Based Materials; 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14, 1989. Veciana, J.; Rovira, C.; Armet, O.; Domingo, V. M.; Crespo, M. I.; Palacio, F. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 77–84.

interact ferromagnetically.[3] The most suitable model for the design of high-spin molecules is based on so-called "topological degeneration"[4,5] and consists of nondisjoint alternant hydrocarbons (AH)[6] with singly occupied nonbonding molecular orbitals (NBMO). For this type of orbital theory predicts a ground open shell spin state, the highest multiplicity being promoted by the ferromagnetic coupling between adjacent NBMO.[4,5] This model theoretically permits, in a given molecule, the stabilization of a ground state having as many unpaired electrons as resulting NBMO's.

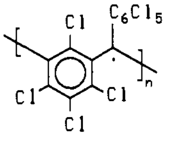
Up to now, not many and yet very unstable species have been tested within this model.[7] In this sense, the series of poly(phenylcarbene)s in which phenylcarbenes are coupled in the *meta* position provides a remarkable example of organic molecules with high-spin ground states. Species with spin as high as $S = 5$ (i.e., undecet spin multiplicity) have been prepared, this being the highest spin multiplicity known to date in organic molecules.[4d] However, since such substances lack enough stability for many practical purposes,[3,4,7] it would therefore be very desirable to obtain new molecules possessing both high spin and stability. Such molecules would be invaluable since they would allow studies otherwise inaccessible or very difficult and because stability is a requirement for the potential applications of these materials.

In this series of papers we will focus our attention on the challenging purpose of obtaining stable molecules having as many unpaired electrons as possible in the ground state. We plan to follow a strategy inspired in a proposal given by Mataga and Ovchinnikov several years ago.[5b] These authors suggested as potential organic ferromagnets two polymers containing the Schlenk biradical[8] and the Leo triradical[9] as building blocks. The synthesis of these polymers has so far proved to be inaccessible, in part because of the high instability of the radical involved. However, taking into account that highly chlorinated di- and triarylmethyl radicals possess high persistance and can be prepared through controlled reactions,[10] our final goals are the polymeric materials of types **1** and **2**.

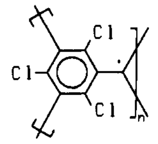
Scheme I



Methods: (a) CHCl$_3$, AlCl$_3$; (b) C$_6$HCl$_5$, AlCl$_3$; (c) exc. (C$_4$H$_9$)$_4$N$^+$ OH$^-$, THF , 3 days ; (d) exc. p-chloroanil ; (e) NaNH$_2$, 18-crown-6, THF, 18 h., or 2.1 eq. (C$_4$H$_9$)$_4$N$^+$ OH$^-$, THF, 3 h., or 1.1 eq. (C$_4$H$_9$)$_4$N$^+$ OH$^-$, THF. 18 h.



1



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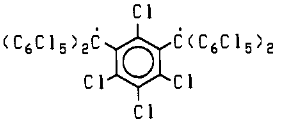

3

To test the feasibility of our final objective, we have prepared biradical **3** and studied, both in solution and in the solid state, its physical, chemical, and structural properties. The study of the ground state of molecule **3** is crucial, since it is the building block of polymer **1**.

Perchlorotriphenylmethyl radical has a propeller-like conformation whose high congestion of *o*-chlorine atoms gives rise to a resolvable pair of enantiomers differing only in the sense of their helicities.[10b,11] Consequently, several stereoisomeric propeller forms are also expected for biradical **3**, due to the restricted rotation of its aryl groups. Until now the effect of such isomerism in high-spin molecules has never been assessed, basically due to the intrinsic instability of these molecules. Only in a very few cases indirect evidence of such isomerism have been given.[12] In the present paper, we report for the first time the separation of nondisjoint AH stereoisomers and the influence of the symmetry and the lack of planarity on their magnetic properties.

Results and Discussion

Syntheses. Tetraphenyl-*m*-xylene **4**, precursor of tetraphenyl-*m*-xylylene biradical **3**, was synthesized by adapting the method previously used to prepare poly(chlorotriphenylmethane)s.[13] The Friedel–Crafts stepwise alkylation of

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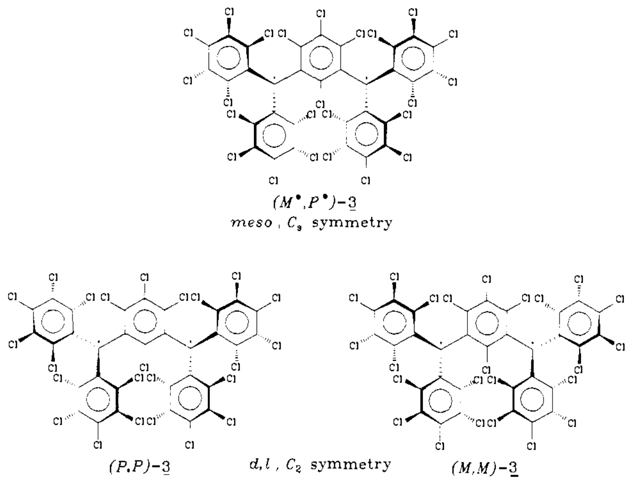
Chart I



1,3,4,5-tetrachlorobenzene outlined in Scheme I leads to tetraphenyl-*m*-xylene **4**.

Biradical **3** was prepared from **4** in a "one-pot" reaction by treatment with an excess of base (n-$Bu_4N^+OH^-$ aq) in THF, followed by oxidation of the resulting dicarbanion with *p*-chloranil. Reducing the excess of the base or the reaction time in the first step of this one-pot reaction (Scheme I) allows control of the formation of the corresponding monocarbanion and, therefore, obtainment, in the second step of pure monoradical **6**. This result is ascribed to the stabilization of the dianion due to the electronic effects of chlorine substituents and the cross-conjugation produced by its topology. It is worth mentioning the use of this rather weak base in the generation of the dianion derived from **4**, since the formation of π-delocalized dianions usually requires stronger bases.[14,15] Both monoradical **6** and biradical **3** were isolated as deep red solids completely stable in ambient conditions for months. As occurs with poly(chlorotriphenylmethyl) radicals,[10,16] solutions of **3** and **6** decompose when exposed to UV or visible light. However, if compared with most radicals of this type, solutions of biradical **3** show an anomalous behavior since it decomposes slowly even in the dark. For this reason, together with biradical **3** is always obtained an impurity (which cannot be completely eliminated even after several recrystallizations in *n*-hexane) (see Figure 1). Although the exact structure of this impurity is not known, its spectral (UV–visible, obtained by the HPLC stopped-flow technique, and ESR, vide infra, spectra)[10] and chromatographic (retention time) characteristics suggest that it has a monoradical nature and, furthermore, that its structure differs from monoradical **6**. The impurity content can be estimated from HPLC chromatograms by assuming molar absorptivities for this monoradical impurity close to those for perchlorotriphenylmethyl radical;[10] the determined values for several samples of biradical **3** are always lower than 1%. This result can be considered irrelevant for most of the studies here presented.

Stereoisomerism in Biradical 3. The analysis of the conformational statics and dynamics of propeller-like molecules in which two or three aryl groups are bonded to a central atom is well established[17,18] and has been confirmed in several experimental studies.[19] In contrast, very few similar studies relative to molecules with two (or more) propeller-like moieties have been reported.[14b,18,20]

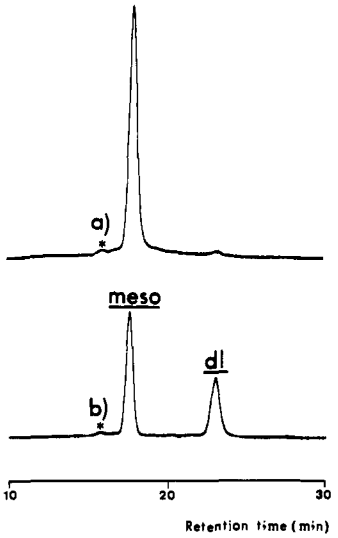


Figure 1. Typical chromatograms at 15 °C of biradical **3** on an ODS column. (a) Microcrystalline sample; (b) amorphous solid obtained by a rapid solvent evaporation. The peak marked with an asterisk corresponds to the monoradical impurity.

Molecules of the type Ar_2Z–Ar'–ZAr_2, where the Z atoms are not chiral centers and all four aryl groups (Ar) are the same and possess local C_2 axes coincident with their bonds to Z atoms, contain two stereogenic elements[21] (the propeller helicities of the two Ar_2ZAr' moieties) and therefore exist as $2^2 = 4$ stereoisomeric forms (two *dl* pairs). Degeneracy of one *dl* pair arises whenever the aryl group (Ar′) possesses a local C_2 axis relating both Z atoms. Therefore, biradical **3** must exist in a *meso* and two enantiomeric (*dl* pair) forms with C_s and C_2 symmetries, respectively. Such stereoisomers differ in the conformations of the propeller-like moieties: (P^*,M^*), (P,P), and (M,M) for the meso and the two enantiomeric forms (Chart I).[22]

The bulky *o*-chlorine atoms of perchlorotriphenylmethyl radical hinder the correlated rotation of its three aryl groups preventing a rapid enantiomeric interconversion at ambient temperature.[11] Since similar steric hindrance is expected for biradical **3**, the resolution of its stereoisomers was envisaged as feasible.

(a) Separation and Enrichment of Stereoisomers. A rapid solvent evaporation of biradical **3** solutions afforded an amorphous solid containing a mixture of *meso* and *dl* isomers. Separation of the isomers was achieved by HPLC on a reversed-phase (octadecylsilane, ODS) column operating at low temperature (15 °C) and using CH_3CN/THF (80:20) as the eluent (Figure 1). In this achiral packing material the *meso* isomer was eluted first, $k'_m = 9.9$, followed by the racemic, $k'_{dl} = 13.2$.[23] These diastereoisomers were unambiguously identified by their characteristic ESR lines (see Electron Spin Resonance Studies). An attempt to resolve the enantiomers of **3** by HPLC on a column packed with (+)-poly(triphenylmethyl methacrylate)[24] was unsuccessful

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(22) Descriptors *P* and *M* denote plus and minus, the rotatory characteristic of a helix, and the star describes the relative conformation. See: Rules for the Nomenclature of Organic Chemistry, IUPAC (Organic Chemistry Division), Commission of Nomenclature of Organic Chemistry, prepared by Cross, I. C., and Klyne, W. *Pure Appl. Chem.* **1976**, *45*, 11–30.

(23) k' denotes the chromatographic capacity factors obtained under the described experimental conditions. $k' = (t_R - t_M)/t_M$, where t_R and t_M are the compound's retention time and the dead time, respectively.

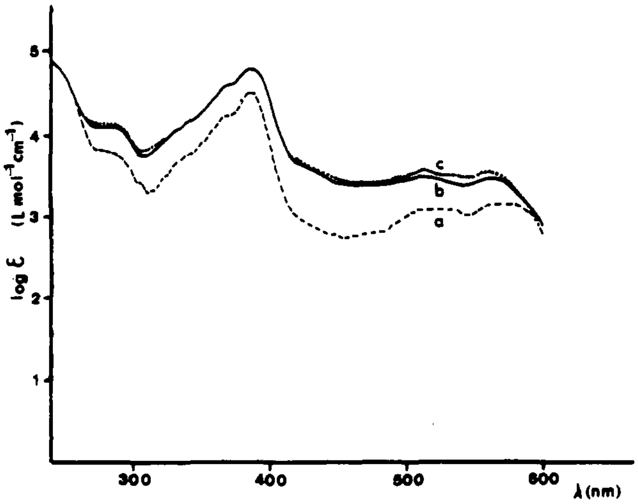


Figure 2. Electronic absorption spectra in $CHCl_3$ of (a) monoradical **6**, (b) pure *meso* isomer of biradical **3**, and (c) equilibrated mixture of *meso* and *dl* isomers of biradical **3**.

due to the poor solubility of **3** in MeOH or *i*-PrOH/*n*-hexane mixtures, the eluents in which the chiral packing material has proved to be effective in the enantiomeric resolution of related compounds.[11,19d]

Recrystallization of **3** from *n*-hexane gave a microcrystalline material identified as the 0.5:1 *n*-hexane clathrate of the pure meso isomer of **3**.[25] Figure 1 shows the diastereoisomer enrichment achieved with this stereoselective procedure.

The interconversion of the *meso* and *dl* stereoisomers in solution can be evidenced by HPLC variable-temperature experiences. Effectively, while if the chromatographic separation of a diastereoisomeric mixture is performed at room temperature a distorted chromatographic profile is obtained, when the temperature is lowered to 15 °C, two base-line separated peaks are obtained (see Figure 1b).[26] Such behavior is characteristic of an on-column interconversion process between two resolvable compounds which takes place during the separation time scale.[27] Therefore, the two diastereoisomeric forms are interconverted in solution with a somewhat low energy barrier.

(b) Characterization by Electronic Spectroscopy of Diastereoisomers. UV–visible absorption spectra of both diastereoisomers, obtained at low temperature by the stopped-flow technique at the chromatographic peak maxima, are characteristic of highly chlorinated triphenylmethyl radicals.[10b,28] They display the radical character bands at 563 (weak), 513 (weak), 387 (intense), and 368 (sh, intense) nm, as well as the absorptions due to the benzenoid character. As occurs in *m*-xylylene biradical,[29] the radical-character absorptions of **3** are associated with four one-electron transitions, involving the two singly occupied π-nonbonding levels and some doubly occupied π-MO and their virtual π* counterparts, which corresponds to the four first excited-state configurations. In addition, the bands in the spectra of both isomers have positions similar to those of the reference monoradical **6**, their molar absorptivities are about twice those of the reference monoradical **6**, and the two first radical-character bands have low intensities while other radical absorptions are intense (Figure 2). These results are consistent with theoretical calculations performed in *m*-xylylene biradicals and benzyl-type monoradicals where the two first one-electron transitions, involving doublet states for monoradicals and triplet states for biradicals, are close in energy and have very low oscillator strengths.[29]

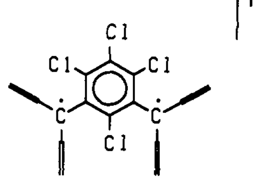
Table I. Kinetic and Thermodynamic Parameters for the Diastereomerization of Biradical **3** in CH_3CN/THF (70:30)

temp, °C	K $(dl/meso)^a$	$k \times 10^5$, s^{-1}: *meso* → $d(l)$	$k \times 10^5$, s^{-1}: $d(l)$ → *meso*	$\Delta G^\ddagger$, kJ mol^{-1}: *meso* → $d(l)$	$\Delta G^\ddagger$, kJ mol^{-1}: $d(l)$ → *meso*
14.5	0.68	0.94	1.39	97.8	97.0
19.5	0.62	2.02	3.31	97.8	96.6
24.5	0.62	3.30	5.36	98.3	97.1
29.5	0.66	6.46	9.80	98.3	97.4
35.5	0.64	15.3	24.0	98.1	97.0
40.0	0.67	22.0	32.9	98.6	97.6

[a] Apparent equilibrium constant.

The molar absorptivities of biradical **3** are not significantly affected by its conformations [$\epsilon_{meso}(\lambda) = \epsilon_{dl}(\lambda)$] as ascertained from the following observations: (a) the normalized absorbances (A_λ/A_{383}) of pure isomers are, within experimental error, very alike and (b) the absorbances of several mixtures with different isomeric molar ratios are coincident. The ratio of molar absorptivities, $\epsilon_{dl}/\epsilon_{meso}$, of 1.0 ± 0.04 at any wavelength, together with the base-line-separated chromatographic peaks, allows us to use the HPLC technique to measure the molar ratio of a diastereoisomer mixture. Indeed, we have determined for an equilibrated mixture, in either CH_3CN/THF, toluene, or $CHCl_3$, a *dl*/*meso* ratio of 40:60, indicating that the *meso* form, prevailing in the crystalline state, is also favored in solution.

(c) Interconversion and Relative Stabilities of Diastereoisomers. In propeller-like molecules of Ar_3Z type enantiomerization results from a reversal of the propellar helicity. The lowest energy mechanism for this process is the "two-ring flip", in which two aryl groups rotate in one direction and the third one in the opposite through a conformation where the later ring is perpendicular to the others.[17] Interconversion of *meso* and *dl* isomers in the system under discussion can take place through a similar two-ring flip mechanism. Two operationally distinct processes can be however envisaged: (a) interconversion of *d* (or *l*) and *meso* forms through uncorrelated reversal of the helicities of both propeller-like moieties (epimerization) and (b) interconversion of *meso* and *dl* "phase isomers"[30] (diastereoisomerization of phase isomers). The latter process is analogous to the previously reported one for substituted bis(9-triptycyl)methanes.[30] The phase isomerism in biradical **3** requires strong coupling in the torsional motion of the two propeller-like moieties so that correlated rotations become energetically preferred over uncorrelated ones. This would be the case if the transition state **7**, in which the central phenylene ring is perpendicular to the four external phenyl rings, is electronically stabilized. This transition state corresponds to a correlated double two-ring flip mechanism. The conrotatory motion through this



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[24] Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971–6973.

[25] Highly chlorinated triphenylmethyl radicals act as clathrands due to their molecular bulkiness and limited conformational flexibility. Veciana, J.; Carilla, J.; Miravitlles, C.; Molins, E. *J. Chem. Soc., Chem. Commun.* **1987**, 812–814.

[26] Details of these dynamic–HPLC experiments as well as the determination of the interconversion energy barrier from these experiments will be published elsewhere. For a preliminary account on this topic see: Veciana, J.; Crespo, M. I. *Angew. Chem., Int. Ed. Engl.* **1990**, in press.

[27] Bürkle, W.; Karfunkel, H.; Schurig, V. *J. Chromatogr.* **1984**, 1–14. Melander, W. R.; Lin, H-J.; Jacobson, J.; Horváth, C. *J. Phys. Chem.* **1984**, *88*, 4527–4536 and 4536–4542. Mannschreck, A.; Zinner, H.; Pustet, N. *Chimia* **1989**, *43*, 165–167.

[28] Ballester, M.; Riera, J.; Castañer, J.; Rodriguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498–4505, and references cited therein.

[29] Lejeune, V.; Despres, A.; Migirdicyan, E.; Baudet, J.; Berthier, G. *J. Am. Chem. Soc.* **1986**, *108*, 1853–1860.

[30] We adopt here the term "phase isomers" to describe the residual isomers that are generated by an operation of correlated rotation. Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175–182. For other examples of this type of isomerism see also: Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1438–1448. Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* 1449–1459.

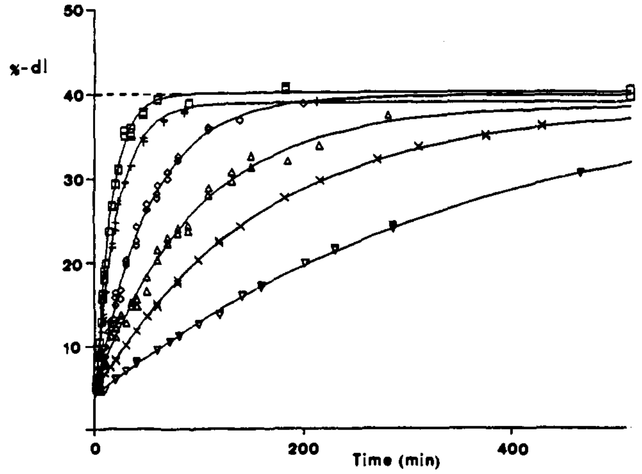

Figure 3. Interconversion of diastereoisomers of biradical **3** in CH_3CN/THF as a function of time at (▽) 14.5, (×) 19.5, (△) 24.5, (◆) 29.5, (+) 35.5, and (□) 40 °C. Continued lines are least-squares fitting of experimental measurements to eq 4 (see Experimental Section). Dashed line is the mean equilibrium composition.

transition state would lead to a $d \rightleftharpoons l$ interconversion, while the disrotatory one to a *meso* $\rightleftharpoons$ *meso* interconversion, giving rise to the phase isomerism. In consequence, the observed *meso* $\rightleftharpoons$ *dl* interconversion would take place through a transition state higher in energy than **7**. We have no direct proof to rule out the process of diastereoisomerization of phase isomers.[31] However, the electronic absorption spectrum of the biradical **3** does not seem to support such a process since no significant bathochromic shift with regard to the reference monoradical **6** has been observed, thus indicating that no significant stabilization of the biradical ground state, and probably of the transition state **7**, occurs. In addition, purely steric contributions do not support the correlated process either, since bulky pentachlorophenyl groups of neighbor propeller-like moieties are arranged in such a way that they do not hinder their uncorrelated motions. Therefore, we consider the independent reversal of the helicities (through a two-ring flip mechanism) of the propeller-like moieties (epimerization) as the most probable process for the observed diastereoisomerization.

The diastereoisomerization rates were determined in a CH_3CN/THF (70:30) solution by starting from a pure sample of the *meso* isomer.[32] A convenient temperature range for the measurements proved to be 14.5–40 °C. The results are summarized in Table I, and the plots of the kinetic experiments are shown in Figure 3. A linear plot of log (k_2/T) vs $1/T$ was used to calculate $\Delta H^{\neq} = 91 \pm 2.5$ kJ mol^{-1} and $\Delta S^{\neq} = -24 \pm 10$ J K^{-1} mol^{-1} and, therefore, $\Delta G^{\neq} = 98 \pm 2.5$ kJ mol^{-1} at 298 K for *meso* → *d* (or *l*) conversion.[33]

The calculated diastereoisomerization barrier value for **3** is very close to that of enantiomerization of perchlorotriphenylmethyl radical ($\Delta G^{\neq}_{303} = 98$ kJ mol^{-1}).[34] This result is in accordance with the similar steric hindrance and the analogous two-ring flip mechanism expected for both compounds, confirming the predictions advanced by Mislow et al.[19c]

The effective equilibrium constant, $K(dl/meso) = [d + l]/[meso]$, observed for the *meso* $\rightleftharpoons$ *dl* process, 0.66 ± 0.04, apparently remains unchanged in the temperature range 14.5–40 °C. This result indicates that the individual equilibrium constants $K(d/meso) = K(l/meso)$[35] are 0.33 and, therefore, in the mentioned temperature range, $\Delta G[meso \rightarrow d] = \Delta G[meso \rightarrow l]$ are ca. 2.5 kJ mol^{-1}; i.e., the *meso* isomer is more populated than the $d + l$ isomers. In addition, this apparently independent K suggests that entropy plays a dominant role in the isomer's relative population. Since no conformers are expected for each of these rather rigid stereoisomers, the contribution to entropy caused by the distinct rotational degrees of freedom of the stereoisomers can be evaluated by symmetry considerations. The symmetry contribution to the entropy is $-R \ln \sigma$, where σ is the symmetry number.[36] Isomer *d* (or *l*) has the symmetry numer 2, whereas σ for *meso* is 1. If this were the only reason taken into account, ΔS [*meso* → *d* (or *l*)] should be $R \ln {}^1/_2 = -5.8$ J K^{-1} mol^{-1}, and therefore a K[*d* (or *l*)/*meso*] value of 0.5 is expected. The mismatching between this value and the experimental one, K[*d* (or *l*)/*meso*] = 0.33, suggests that additional entropic and/or enthalpic terms must also contribute to the higher population of the meso isomer. Since there is no guarantee that the torsional degrees of freedom are identical for the *meso* and *d* (or *l*) isomers, two limit situations can be invoked to explain the experimental results; i.e., either ΔS [*meso* → *d* (or *l*) ≈ −9 J K^{-1} mol^{-1} and ΔH [*meso* → *d* (or *l*)] ≈ 0 or ΔH [*meso* → *d* (or *l*) ≈ 1 kJ mol^{-1} and ΔS [*meso* → *d* (or *l*)] ≈ −5.8 J K^{-1} mol^{-1}.[37] Consequently, ΔH and ΔS values close to those given above should explain the experimental K values as well as their apparent temperature independence in the narrow temperature range studied so far. Unfortunately, attempts to determine the precise ΔH and ΔS values by expanding the measurements of $K(dl/meso)$ at higher temperatures were unsuccessful due to the irreversible decomposition of biradical **3**.

Electron Spin Resonance Studies. (a) Isotropic Spectra. The room temperature spectrum of monoradical **6** in toluene is characteristic of a highly chlorinated triphenylmethyl radical.[10b] It shows an intense symmetrical line at $g = 2.0023$ with a peak-to-peak width, ΔH_{pp}, of 0.156 mT and two pairs of weak ^{13}C satellites with hyperfine coupling constants of 3.09 and 1.22 mT. These satellites arise from the coupling with the magnetically active nuclear spins of ^{13}C atoms in natural abundance at the α and *aromatic* positions. The room temperature spectrum of the equilibrated mixture of *meso* and *dl* isomers of biradical **3** in toluene consists only of two superimposed symmetrical lines centered at $g \approx 2.0024$ with ΔH_{pp} values of 0.16 and 1.25 mT. The narrow line is assigned to the monoradical impurity, while the broad line is ascribed to the isomers of biradical **3**. The large wings of this broad line prevent observation of any of the weak ^{13}C satellite lines expected for both isomers and, therefore, the determination of hyperfine coupling constants for the ^{13}C atoms at the α and *aromatic* positions of the two triphenylmethyl moieties. Thus, from this spectrum neither the spin density distribution nor the relative magnitude of electron exchange interactions (J vs ^{13}C) can be estimated. Nevertheless, the breadth of the line ascribed to the isomers of biradical **3** indicates that the (anisotropic) electron–electron dipolar interactions in the isomers are moderate; i.e., the zero-field splitting parameters, $|D/hc|$, should be in the range 0.003–0.030 cm^{-1}.[38] When the temperature of a biradical **3** sample is lowered, the line corre-

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[31] Observation of the enantiomeric forms of biradical **3** with the same half-life times of the *meso* form would discard the phase isomerism.

[32] Interconversion rates are dependent on the solvent nature; i.e., $k_1(CHCl_3) \leq k_1(CH_3CN/THF) < k_1$(toluene).

[33] The Arrhenius plot gave $E_a = 93 \pm 2.5$ kJ mol^{-1} and log $A = 27 \pm 1.1$ for *meso* → *d*(or *l*) conversion.

[34] Veciana, J.; Crespo, M. I.; Rovira, C.; Mannschreck, A.; Stühler, G. Unpublished results.

[35] In an achiral solvent, the concentrations of both enantiomers must be identical and, therefore, $K[d/meso] = K[l/meso] = K[dl/meso]/2$.

[36] The value of σ is equal to the number of undistinguishable positions adopted by the molecule (considered rigid) by simple rotations. For similar analyses of symmetry contributions to entropy see: Klumpp, G. W. In *Reactivity in Organic Chemistry*; Wiley: New York, 1982; pp 36–50 and references cited therein.

[37] A lower enthalpy for the *meso* isomer could be explained by intramolecular Cl...Cl stabilizing interactions taking place between the four Cl atoms at the ortho positions of C_6Cl_5 rings belonging to different radical centers (see Figure 5). Several examples of similar stabilizing interactions have been previously reported. See: Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222–228. Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308–4314. Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481.

[38] If $|D/hc|$ is smaller than roughly 0.003 cm^{-1}, the anisotropic interaction is averaged out by the Brownian motion so that well-resolved ESR hyperfine spectra can, in principle, be observed. By contrast, if $|D/hc|$ is larger than 0.030 cm^{-1}, the anisotropic contribution to the inhomogeneous line width is so large that the spectrum would have undetectable broad lines. See: Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1986; pp 223–257. Kriste, B.; Krüger, A.; Kurreck, H. *J. Am. Chem. Soc.* **1982**, *104*, 3850–3858.

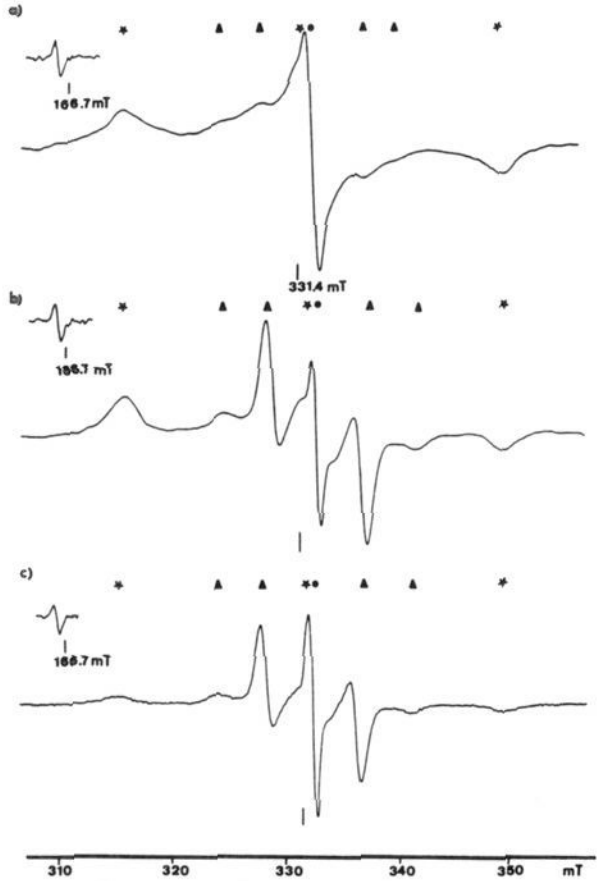

Figure 4. First-derivative ESR spectra in frozen toluene at 140 K of biradical **3** with different diastereoisomeric ratios (determined by HPLC, see text): (a) *meso*-**3**/*dl*-**3** ratio = 98/11; (b) *meso*-**3**/*dl*-**3** = 71/29; (c) *meso*-**3**/*dl*–**3** ratio = 60/40. The symbols ★ and ▲ mark the positions of transitions associated with the triplets *meso*-**3** and *dl*-**3**, respectively. The symbol ● marks the monoradical impurity signal.

sponding to the monoradical impurity remains practically unchanged while large changes are observed for the biradical line.[39] The resulting spectra at low temperature are typical of line-shape effects produced by reorientational motion in triplets with moderate dipolar interactions and high motional correlation times.[40] Thus, the outward appearance of the nonrigid media spectra in the slow-tumbling region is very similar to that of the rigid-limit spectra.

(b) Rigid Media Spectra. As occurs in some highly chlorinated triphenylmethyl radicals,[10b] the spectrum of monoradical **6** in frozen toluene (143 K) appeared to be symmetrical, indicating that the *g* isomer has a low (if any) anisotropy. The ESR spectrum in frozen toluene (143 K) of an equilibrated mixture of the meso and *dl* isomers of biradical **3** gave a series of signals with different intensities as shown in Figure 4c. A careful inspection of this spectrum revealed that it consists of a superimposition of the spectra of three different randomly oriented species: two triplets with different zfs parameters and a monoradical. The four $\Delta m_s = 1$ lines detected at 323.5, 328.1, 336.6, and 341.7 mT (labeled with a ▲ in Figure 4) correspond to the $H_\parallel$ and $H_\perp$ transitions of a triplet with axial symmetry. The three $\Delta m_s = 1$ lines observed at 316.3, 332.4, and 349.0 mT (labeled with a ★ in Figure 4) are ascribed to the $H_{z,x}$ (accidentally degenerated) and H_y transitions of an asymmetrical triplet. The intense structureless line detected in the half-field region, 166.7 mT, is assigned to the $\Delta m_s = 2$ transitions of both triplet species. Finally, the singlet line observed at the center of the spectrum (labeled with ● in Figure 4) corresponds to the monoradical impurity.

Table II. ESR Data of Radical Compounds[a]

	radical		
	6	*meso*-**3**	*dl*-**3**
g_x		2.0023	2.0036
g_y		2.0020	2.0036
g_z		2.0020	2.0024
g_{av}[b]	2.0026	2.0021	2.0032
g_{iso}[c]	2.0023	≈2.0025	≈2.0025
$\lvert D/hc\rvert$,[d] cm^{-1}		0.0152	0.0085
$\lvert E/hc\rvert$,[d] cm^{-1}		0.0051	≤0.0003

[a] In frozen toluene at 143 K unless otherwise indicated. [b] At 298 K in fluid solution at the fast-tumbling region. [c] Determined directly from the rigid-limit spectra (radical **6**) or calculated from $g_{av} = (g_x + g_y + g_z)/3$. [d] The error in each of these values is estimated as ±0.0003 cm^{-1}.

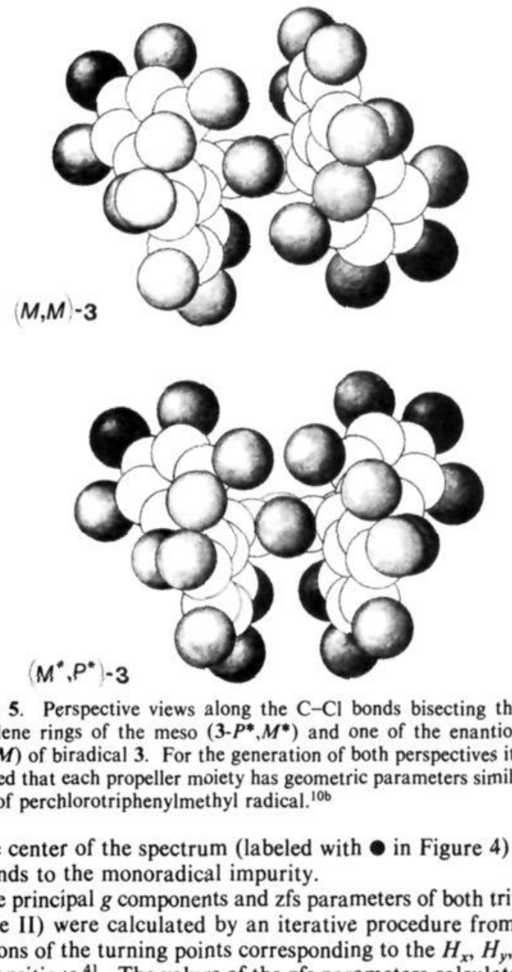

Figure 5. Perspective views along the C–Cl bonds bisecting the *m*-phenylene rings of the meso (**3**-P^*,M^*) and one of the enantiomers (**3**-*M*,*M*) of biradical **3**. For the generation of both perspectives it was assumed that each propeller moiety has geometric parameters similar to those of perchlorotriphenylmethyl radical.[10b]

The principal *g* components and zfs parameters of both triplets (Table II) were calculated by an iterative procedure from the positions of the turning points corresponding to the H_x, H_y, and H_z transitions.[41] The values of the zfs parameters calculated in this way are the same as those obtained by a simulation procedure (vide infra)[42] and, furthermore, are in accordance with the magnitude of the *D* value estimated from the isotropic spectra. The triplet with a three-line ESR fine structure deserves a special mention, since randomly oriented ensembles of triplets generally show either four or six lines. The unusual three-line appearance arises when the E/D ratio is accidentally equal to roughly 1/3. In this case the lines corresponding to H_x and H_z transitions overlap and those corresponding to H_y are moved to the center of the spectrum (see Figure 6a). Very few examples of this special

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(39) Detailed motional ESR experiments with biradical **3** and other structurally related biradicals will be published elsewhere.

(40) Lee, S.; Brown, I. M. *Phys. Rev. B* **1986**, *34*, 1442–1448, and references cited therein.

(41) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772. In this iterative procedure it is assumed that the principal axes of the *D* and *g* tensors are coaxial.

(42) Simulations were performed on an IBM PS2/80 with a FORTRAN program written by some of us, Jullian, N., Crespo, M. I., Veciana, J. The simulation uses the method previously developed by Kottis et al.: Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1963**, *39*, 393–403; **1964**, *41*, 379–393.

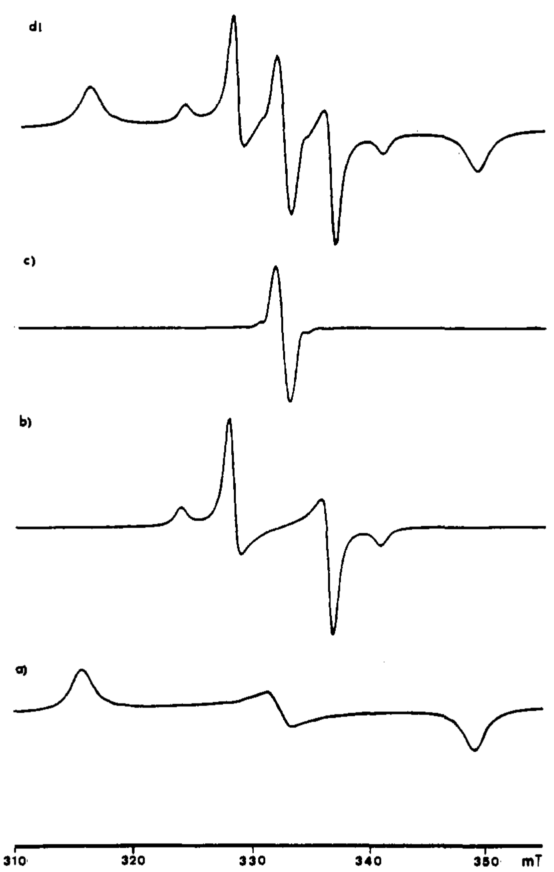

Figure 6. Simulation of the first-derivative ESR spectrum of biradical 3 with a *meso*-3/*dl*-3 diastereoisomeric ratio of 71/29 (see Figure 4b). Theoretical spectra for randomly oriented species: (a) triplet with $|D/hcl|$ = 0.0152 cm^{-1}, $|E/hc|$ = 0.0051 cm^{-1}, and Lorentzian line shape, L.l-s, with a half-width at half-height, Γ, of 0.6 mT; (b) triplet with $|D/hc|$ = 0.0085 cm^{-1}, $|E/hc| \leq 0.0003$ cm^{-1}, and L.l-s with Γ = 0.6 mT; (c) monoradical impurity with g = 2.0023[10] and L.l-s, Γ = 0.3 mT; (d) summation of theoretical spectra a–c. The ratio of intensities of the theoretical spectra a–c is 76:23:1.

situation have been reported so far.[43]

The zfs parameters are a measure of the spin–spin dipolar interaction which in turn depends critically on the distribution of the unpaired spins and the interatomic separations. The D parameter is the most sensitive to the distance between atoms with spin densities, while the E parameter is related to the molecular symmetry. Consequently, zfs parameters of related triplets can be used to give precise structural assignments on the basis of their relative D and E values. The perspective views expected for the meso (3-*P**,*M**) and one of the enantiomeric (3-*M*,*M*) forms of biradical 3 are shown in Figure 5, where the relative dispositions of the four pentachlorophenyl rings are clearly visualized. In the *meso* isomer two phenyl rings belonging to different radical centers are rather close and nearly parallel, whereas in the *d* (or *l*) isomer all the phenyl rings are far away from each other. Since some spin density must be located on these rings,[44] a shorter average separation of the unpaired electrons and a larger interaction between them are expected for the meso isomer. Therefore, the triplet with the largest D value (and a no-null E parameter) is assigned to the *meso* isomer and the triplet and the smallest D value (and null E parameter) is ascribed to the pair of enantiomers (*dl* pair) of biradical 3. In addition, such an assignation is in accordance with the low symmetry of the *meso* form (C_s symmetry) for which the largest E value is expected.

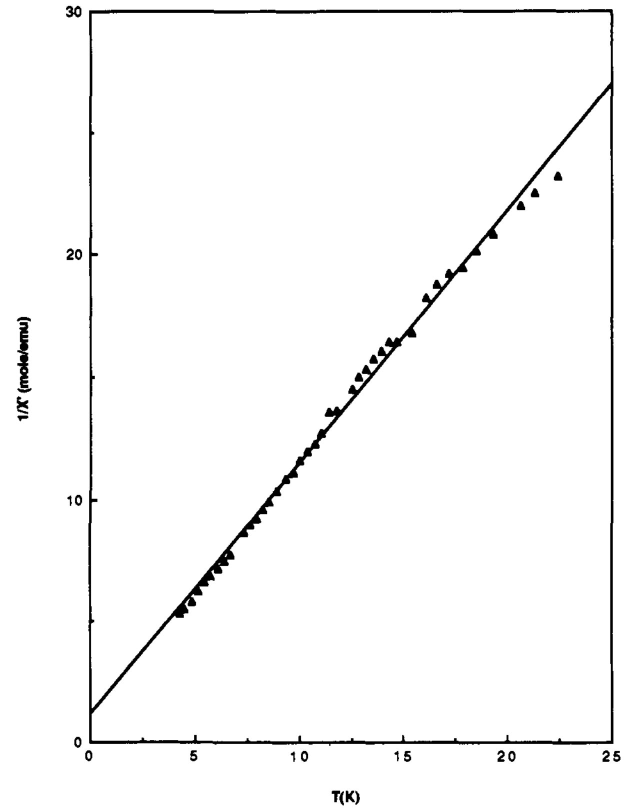

Figure 7. Temperature dependence of paramagnetic susceptibility, χ^{-1} vs T, of the *meso* isomer of biradical 3.

To give an unequivocal assignation of the conformation of the most stable diastereoisomer, the ESR spectra of several mixtures with different diastereoisomeric ratios were taken. Figure 4 shows three representative examples from which it is concluded that the triplet with a higher stability is that with the largest D value, i.e., the *meso* form. An additional confirmation was achieved by simulation of the spectra corresponding to those mixtures. The simulated spectrum corresponding to a 71:29 mixture of the *meso* and *dl* isomers (as determined by HPLC) is given in Figure 6. This simulation is the result of adding the three theoretical spectra of two triplets and one monoradical (the g, D, and E values used are those given in Table II). The relative intensities of the three theoretical spectra required to achieve a good agreement with the experimental spectrum (Figure 4b) were 76:23:1. These values are in agreement with the experimentally determined diastereoisomeric ratio.

The variation of the ESR signal intensity of the $\Delta m = 2$ line with temperature was studied in two enriched samples containing 89% *meso*-3 and 84% *dl*-3, respectively.[45] The measurements were obtained upon first decreasing and then increasing the temperature to demonstrate that the intensity changes are reversible. We found that both samples follow the Curie law $I = C/T$ (r = 0.997–8) over the temperature range 130–188 K.[46] These results indicate that in both stereoisomers, irrespective of their symmetries, the triplet is the ground state.[47] They also show

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(43) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146–5147. Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 2788–2790.

(44) Although the exact spin density distributions for the two diastereoisomeric biradicals are not known, the observed values for the D parameters can give an insight about such distributions. Assuming the point dipole approximation, D (in mT) = $2789/R$ (in Å),[3] the average distances between the unpaired electrons for both biradicals were estimated to be 5.5 and 6.7 Å. Since both values are clearly larger than the distance between the two α carbons, 4.8 Å, the unpaired electrons must not be totally localized on such carbons but also reside on the chlorinated phenyl and phenylene rings.

(45) The *dl*-enriched sample was obtained from an equilibrated mixture of 3 by an HPLC separation at a semipreparative scale. Solvent (THF/CH$_3$CN) of the fractions containing the *dl* isomer was eliminated under vacuum at low temperature and replaced with cold toluene.

(46) Studies in toluene with pure *meso* and *dl* isomers have not so far been performed since the rate of isomerization in this solvent[32] is rather high and interconversions take place during the manipulation of the samples. However, the identical results obtained with both enriched samples permit us to expect similar results for the pure isomers.

that the strong deviations from planarity expected for this nondisjoint AH do not produce perturbations on its π-conjugated system strong enough to cause either degeneration or inversion in the first two low-lying states (singlet and triplet). Therefore, the use of the current theories for the prediction of ground-state multiplicities[5,6,48] in related AH fits well, even in those cases which lack planarity.

Magnetic Susceptibility and Magnetization Studies. The ac magnetic susceptibility of biradical **3** was measured in the temperature range 4.2–25 K. Both in-phase, χ', and out-of-phase, χ'', components of the susceptibility were recorded, although no significant values of χ'' were observed. The measurements were initially made by using the pure *meso* isomer of **3** (0.5:1 *n*-hexane clathrate of **3**), although no differences are observed when a sample composed of a 60:40 mixture of meso and *dl* isomers is used.

The $1/\chi'$ vs T plot gives a straight line in the whole temperature range as shown in Figure 7. A good fit of the data to a Curie–Weis law, $\chi = C/(T - \Theta)$, was found for $C = 0.97 \pm 0.02$ emu K/mol and $\Theta = -1.1$ K. The value of the Curie constant corresponds to $\mu_{\text{eff}} = 2.78\ \mu_B$. Since $\mu_{\text{eff}} = g[S(S + 1)]^{1/2}$ and $g = 2.0021$, as determined from ESR experiments, the effective spin number is $S = 0.98 \pm 0.01$. This value is in good agreement with the theoretical one expected for a triplet ground state $S = 1$ and furthermore is consistent with the presence of a small amount (ca. 1%) of a monoradical ($S = {}^1/_2$) impurity. The small Θ value indicates that the interaction taking place between triplet molecules is either not significant or slightly antiferromagnetic.

In the temperature range 80–300 K the susceptibility measurements taken with a Faraday balance confirmed the low-temperature results obtained for both the pure meso isomer and the *meso*/*dl* mixture, indicating that both isomers have triplet ground states. These results also indicate that thermal excitations at room temperature are not energetic enough to populate their first excited singlet states which, therefore, must be located several kilojoules apart from the ground state.

Magnetization of biradical **3** was measured at 4.2 K as a function of magnetic field in the range 0–5 T. The results, expressed in Bohr magnetons, are plotted vs temperature-normalized field strength in Figure 8. The same plot shows the chart of the theoretical general equations for the magnetazation of paramagnets with $S = {}^1/_2$, 1, and ${}^3/_2$,[49] $M = NgS\mu_B B_s(\eta)$, where $B_s(\eta)$ is the Brillouin function and $\eta = g\mu_B H/(k_B T)$. The experimental data follow rather well the curve corresponding to a spin value of 1, in good agreement with the susceptibility results.

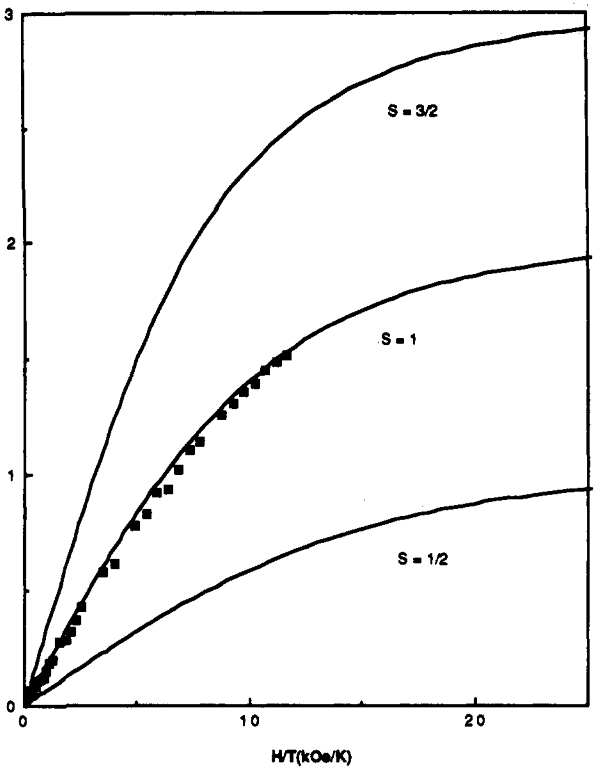

Figure 8. Plots of calculated magnetization per mole, $M/N\mu_B$, vs the ratio of the magnetic field over the absolute temperature, H/T, for isolated $S = {}^1/_2$, 1, and ${}^3/_2$ species with $g = 2.0021$. The squares correspond to experimental measurements of the *meso* isomer of biradical **3**.

Experimental Section

General Methods. ^{1}H NMR spectra were taken on Bruker WP 80 SY instrument. Chemical shifts values (δ) are reported in ppm downfield from internal tetramethylsilane. ESR spectra were recorded on a Varian E-line Century Series X-Band ESR spectrometer equipped with a field frequency lock, a variable-temperature accessory, and a data acquisition system. g values were determined by the usual procedure using a T_{104} dual-sample cavity with DPPH as standard.[50] The reported ESR spectra were obtained at microwave frequencies in the vicinity of 9.15 GHz with the 100-kHz field modulation detection unit. All precautions were taken to avoid undesirable spectral line broadening such as that arising from microwave power saturation and magnetic field overmodulation. The samples were degassed by three freeze (liquid N_2)–pump–thaw (dry ice/acetone) cycles and sealed under prepurified dry argon atmosphere. UV–vis and IR spectra were measured on Perkin-Elmer Lambda Array 3840 and Perkin-Elmer 682 spectrometers, respectively. Analytical HPLC was performed on a ODS column (0.46 × 15 cm) with a flow rate of 1.0 mL min^{-1} of CH_3CN/THF (80:20) on a Perkin-Elmer Series 3DLC equipped with a Sigma 15 data station and a LC-75 spectrophotometer detector operating at 383 nm. The column was thermostated at low temperature (15 °C) with a home-made jacket using a Hetofrig ultrathermostat with external cirulation. On-line UV–vis spectra were registered by adapting the column outlet to a 8-μL LC Micro Flow cell and using the Lambda Array 3840 spectrophotometer. Semipreparative HPLC was performed on a ODS column (1.0 × 25 cm) with a flow rate of 5 mL min^{-1} of CH_3CN/THF (88:12) using the same equipment as for the analytical experiments. Preparative chromatography under flash conditions[51] employed 230–400-mesh silica (SDS, silica gel 60). Melting points were obtained with a Köfler microscope. DSC and TG analyses were done with Perkin-Elmer DSC-2 and TG-1 instruments, respectively. Microanalyses were performed at the Microanalysis Service of the Centre d'Investigació y Desenvolupament, CSIC. THF and toluene were distilled from benzophenone ketyl under argon immediately before use. Reagents and solvents were obtained commercially and used without further purification unless otherwise noted. Solvents for chromatography and optical spectrosopic studies were of spectro grade. The handling of radicals in solution was performed in the dark.

Preparation of $\alpha,\alpha,\alpha',\alpha'$,2,4,5,6-Octachloro-*m*-xylene (5). A mixture of 1,3,4,5-tetrachlorobenzene (7.24 g, 33.0 mmol), $CHCl_3$ (150 mL), and powdered anhydrous $AlCl_3$ (4.3 g, 33.0 mmol) was refluxed for 9 h with stirring in dry atmosphere and then poured into cracked ice–hydrochloric acid. The organic layer was decanted, washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. The residue was submitted to flash chromatography (hexane) to give **5** as a white powder (7.82 g, 61%): mp 108–110 °C (lit.[52] mp 94–96 °C); ^{1}H NMR [CCl_4/$(CD_3)_2CO$] δ 7.8 (br s). Anal. Calcd for $C_8H_2Cl_8$: C, 25.16; H, 0.53; Cl, 74.31. Found: C, 25.17; H, 0.45; Cl, 74.30.

2,4,5,6-Tetrachloro-$\alpha,\alpha,\alpha',\alpha'$-tetrakis(pentachlorophenyl)-*m*-xylene (4). A mixture of **5** (1.20 g, 3.0 mmol), pentachlorobenzene (5.0 g, 20 mmol), and powdered anhydrous $AlCl_3$ (1.0 g, 7.5 mmol) was heated at 140 °C (6 h) in a glass pressure vessel. The resulting mass was poured into cracked ice–hydrochloric acid and extracted with $CHCl_3$. The organic extract was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. The residue was subjected to flash chromatography (hexane) to give unreacted pentachlorobenzene (1.4 g), αH-pentadecachlorotriphenylmethane[53] (0.83 g), and **4** as a white solid (1.53 g, 36%): mp > 320 °C; ^{1}H NMR ($CDCl_3$) δ 6.75–6.99 (m); IR (KBr) 2920, 1529, 1360, 1335, 1330, 1304, 1289, 1185, 810, 804, 786 cm^{-1}; UV ($CHCl_3$)

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(47) The Curie plots are such that linear plots would also be possible if the singlet–triplet splittings were 400 J/mol or less. However, this possibility is ruled out by the quantitative measurements of the effective magnetic moments of biradical **3** in the solid state.

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242 nm, 235 (sh), 294, 304 (ε, 96 900, 63 300, 2160, 2150) nm. Anal. Calcd for $C_{32}H_2Cl_{24}$: C, 31.05; H, 0.16; Cl, 68.79. Found: C, 31.18; H, 0.16; Cl, 68.62.

2,4,5,6-Tetrachloro-*α,α,α′,α′*-tetrakis(pentachlorophenyl)-*m*-xylyl Radical (6). (**a**) Sodium amide (0.03 g, 0.9 mmol) and 18-crown-6 (0.23 g, 0.9 mmol) were added, under argon and in the dark, to a suspension of **4** (0.23 g, 0.19 mmol) in THF (30 mL), and the resulting mixture was stirred at room temperature (18 h). Then, *p*-chloranil (0.31 g, 1.26 mmol) was added and the stirring continued (1 h). Elimination of the solvent gave a residue which was passed through silica gel (hexane) to give **6** as a wine red microcrystalline solid (0.22 g, 96%): mp 305–306 °C; IR (KBr) 2923, 1528, 1503, 1363, 1350, 1329, 1307, 1293, 1253, 810, 800, 793 cm^{-1}; UV–vis ($CHCl_3$) 285, 367 (sh), 386, 480 (sh), 513, 564 (ε, 6940, 18 670, 34 640, 1150, 1200, 1270) nm; EPR (toluene) *g*, 2.0032 ± 0.0003, ^{13}C–*α* = 3.09 mT, ^{13}C–arom = 1.22 mT. Anal. Calcd for $C_{32}HCl_{24}$: C, 31.10; H, 0.08; Cl, 68.84. Found: C, 31.38; H, 0.35; Cl, 68.79. Magnetic Suscept. (80–300 K): χ_d, -640×10^{-6} emu mol^{-1}; Θ, −1 K; μ_{eff}, 1.69 μ_B.

(**b**) Tetrabutylammonium hydroxide (40% in water) (0.27 mmol) was added, under argon and in the dark, to a suspension of **4** (0.15 g, 0.12 mmol) in THF (30 mL), and the resulting mixture was stirred at room temperature (3 h). Then, *p*-chloranil (0.079 g, 0.32 mmol) was added and the stirring continued (2 h). Elimination of the solvent gave a residue which was passed through silica gel (CCl_4) to give **6** as a wine red microcrystalline powder (0.147 g, 98%): UV–vis ($CHCl_3$) 285, 367 (sh), 386, 480 (sh), 513, 564 (ε, 6900, 19 600, 36 100, 1220, 1290, 1350) nm. Magnetic Suscept. (80–300 K): μ_{eff}, 1.82 μ_B.

(**c**) The preceding reaction (**b**) was repeated by using 0.12 mmol of **4**, 0.14 mmol of base with a reaction time of 18 h and 0.17 mmol of *p*-chloranil. Radical **6** (0.145 g, 96%) was also obtained: UV–vis ($CHCl_3$) 285, 367 (sh), 386, 480 (sh), 513, 564 (ε, 7080, 18 500, 35 100, 1140, 1220, 1260) nm. Magnetic Suscept. (80–300 K): μ_{eff}, 1.74 μ_B.

2,4,5,6-Tetrachloro-*α,α,α′,α′*-tetrakis(pentachlorophenyl)-*m*-xylylene Biradical (3). A great excess of tetrabutylammonium hydroxide (40% in water) (10 mmol) was added, under argon and in the dark, to a suspension of **4** (0.25 g, 0.21 mmol) in THF (60 mL), and the resulting mixture was stirred at room temperature (3 days). Then, *p*-chloranil (1.6 g, 6.5 mmol) was added and the stirring continued (3 h). Elimination of the solvent gave a residue which was passed through silica gel (CCl_4) to give **4** (*meso* and *dl* isomers in a 60:40 ratio, as ascertained by HPLC) as a wine red solid (0.24 g, 96%): mp > 320 °C dec.; IR (KBr) 1510, 1490, 1340, 1325, 1318, 1310, 1280, 1260, 1232, 820, 803 cm^{-1}; UV–vis ($CHCl_3$) 282, 368 (sh), 387, 481 (sh), 513, 563 (ε, 13 116, 37 670, 61 830, 2430, 2872, 2727) nm. Anal. Calcd for $C_{32}Cl_{24}$: C, 31.11; Cl, 68.88. Found: C, 31.19; Cl, 68.75. Magnetic Suscept. (80–300 K): μ_{eff}, 2.83 μ_B. Recrystallization from *n*-hexane gave the pure *meso* isomer as a clathrate with *n*-hexane (HPLC), red microcrystalline powder (0.15 g) mp (DSC-TG) 180 °C dec[54]: IR (KBr) 2958, 2922, 1510, 1490, 1340, 1325, 1318, 1310, 1280, 1260, 1232, 820, 803 cm^{-1}; UV–vis ($CHCl_3$) 282, 368 (sh), 387, 481 (sh), 513, 563 (ε, 12 417, 37 660, 62 778, 2380, 2873, 2817). Anal. Calcd for $C_{32}Cl_{24}\cdot{}^1/_2C_6H_{14}$: C, 32.86; H, 0.59; Cl, 66.58. Found: C, 32.76; H, 0.51; Cl, 66.50. Magnetic Suscept. (80–300 K): χ_d, -660×10^{-6} emu mol^{-1}; Θ, −1 K; μ_{eff}, 2.87 μ_B.

Kinetic Measurements. The rates of isomerization were measured in the temperature range 14.5–40 °C for a solution of *meso* isomer of biradical **3** in THF/CH_3CN (30:70) (ca. 0.0348 mg mL^{-1}, ca. 0.0272 mM). At each temperature, small glass ampules (ca. 1 cm i.d. and 5 cm long) containing the solution were immersed in a thermostated bath. The temperature was considered to be accurate within ±0.2 °C. After a given period of time (a few minutes to several hours), they were taken out of the bath and cooled in dry ice/acetone to quench the isomerization reaction.

Analyses of the *dl* and *meso* isomer molar fractions, x_{dl} and x_m, were determined by analytical HPLC using

$$x_{dl} = A_{dl}/(A_m\epsilon + A_{dl}) \tag{1}$$

$$x_m = A_m/(A_m\epsilon + A_{dl}) \tag{2}$$

where $\epsilon = \epsilon_{dl}/\epsilon_m$ is the ratio of molar absorptivities at 382 nm and A_{dl} and A_m are the integrated absorbances of *dl* and *meso* isomers at the same wavelength. The experimental ε value was 1.00 ± 0.04. The analytical HPLC determinations were performed at low temperature (15 °C) to avoid on-column interconversions between the *dl* and *meso* isomers.

The analysis of rate data was carried out according to eqs 3 and 4 by assuming that the diastereoisomerization process takes place through uncorrelated reversal of the helicities of the stereogenic centers (epimerization)[55]

$$d \underset{k_2}{\overset{2k_1}{\rightleftharpoons}} meso \underset{2k_1}{\overset{k_2}{\rightleftharpoons}} l \tag{3}$$

$$x_{dl} = K/(K + 1) + [1/(K + 1) - x^\circ{}_m] \exp[-2k_1(K + 1)t] \tag{4}$$

where, k_1, $K = k_2/k_1$, and $x^\circ{}_m$ are, respectively, the rate constants for isomerization from *d* (or *l*) to *meso* isomer, the apparent equilibrium constant defined as $x^\infty{}_{dl}/x^\infty{}_m$ (molar fraction at infinite time), and the *meso* molar fractions at $t = 0$. Statistical factors of 2 must be taken into account in eq 3 since the probability of the *d* (or *l*) → *meso* process is twice as large as the probability of the *meso* → *d* (or *l*) process. In most experiments $x^\circ{}_m$ differed from 1.0 ($x^\circ{}_m$ = 0.95–0.99) since partial diastereoisomerization of pure *meso* isomer takes place during dissolution of the solid sample. A least-squares treatment of eq 4 gave the k_1, k_2, K, and $x^\circ{}_m$ values at each temperature. ΔG^* values reported in Table I were calculated from k_1, k_2, and temperature values with the Eyring equation.[56]

Equilibration Measurements. To obtain the *dl*/meso ratios in THF/CH_3CN (30:70) at infinite time, i.e., the apparent equilibrium constants $K(dl/m)$, the solutions were subjected to continued heating for at least several half-lives in the temperature range 14.5–40 °C. When isomerization was very slow, i.e., long periods of time are needed to achieve complete equilibrium, partial decomposition was observed. The value of $K(dl/m)$ was found to be apparently constant, within experimental error, in the studied temperature range. The value of $K(dl/meso)$ = 0.67 ± 0.02 was found to be the same as that calculated from the kinetic measurements (0.65 ± 0.02, Table II) and, moreover, it agrees with the *dl*/*meso* ratio of 0.67 present in a freshly synthesized sample of biradical **3**.

Magnetic Measurements. Magnetic susceptibility data were measured, using the Faraday technique, from 80 to 300 K with a Varian 4-in. magnet with constant-force caps and a Cahn RG electrobalance. The measurements were made on samples (ca. 0.01–0.03 g) of monoradical **6** and biradical **3**. The observed magnetic susceptibilities, χ, were fitted to the Curie–Weiss law, $\chi - \chi_d = C/(T - \Theta)$ by a least-squares method. This procedure allows determination of the molar diamagnetic susceptibilities of monoradical **6** and biradical **3**. The effective magnetic moments, μ_{eff}, were calculated from the Curie constant by using the relationship[49] $\mu_{eff} = (C/0.125)^{1/2}$.

ac susceptibility measurements were carried out in a computer-controlled susceptometer[57] in the temperature range 4.2–25 K. The measurements made on samples (ca. 0.04 g) of biradical **3** were performed at zero external field, the amplitude of the alternating magnetic field being 1 Oe and the frequency 122 Hz. The molar diamagnetic susceptibility of biradical **3**, as determined at high temperatures, is about 1.5% of the lowest measured value of χ in these experiments, falling within experimental error. Consequently, the diamagnetic contribution of the molecule was not considered to be relevant in the 4.2–25 K temperature range and was not subtracted from the experimental data. Magnetization measurements at 4.2 K were made, using the same equipment, by integrating the voltage induced in the secondary coils when the sample was moved in the presence of an external magnetic field.

Summary and Conclusions

A nondisjoint alternant hydrocarbon (AH), biradical **3**, and the corresponding monoradical **6** have been synthesized and isolated as stable solids at ambient conditions. For the first time, two stereoisomers of a nondisjoint AH have been separated and characterized. Their chemical, spectroscopic, and magnetic properties have been studied. Kinetic and thermodynamic studies of their interconversions have also been carried out. The following conclusions are derived:

(1) According to conformational analysis, biradical **3** exists in two diastereoisomeric forms (*meso*-**3** and *dl*-**3**) which are rather stable due to restricted rotation of the aryl groups.

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[54] Concomitant declathration and decomposition is observed.

[55] Should the interconversion mechanism be the diastereoisomerization of phase isomers, the process at the time scale of the observation must be analyzed in terms of eqs 3′ and 4′. The analysis of rate data using eq 4′ gives

$$dl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} meso \tag{3′}$$

$$x_{dl} = K/(K + 1) + [1/(K + 1) - x^\circ{}_m] \exp[-k_1(K + 1)t] \tag{4′}$$

rate constants, k_1 and k_2, that are twice as large as those found with eq 4, while identical K and $x^\circ{}_m$ are obtained. Consequently, differences in the diastereoisomerization mechanism only have influence on the activation entropy and do not affect the activation enthalpy.

[56] The transmission coefficient was assumed to be unity.

[57] Rillo, C. Ph.D. Thesis, University of Zaragoza, Spain, 1986.

(2) Both diastereoisomers are obtained in a *meso/dl* ratio of 60:40. However, recrystallization of the mixture results in the pure meso form.

(3) The diastereoisomerization barrier of $meso \rightarrow d$(or l) (98 kJ mol^{-1}) is similar to that of a related monoradical as could have been inferred from the analogy of their steric hindrances and interconversion two-ring flip mechanisms expected for both compounds.

(4) The obtained ESR spectra (zfs parameters) are consistent with the C_s and C_2 symmetries expected for *meso*-**3** and *dl*-**3**, respectively.

(5) The diastereoisomers have both in solution and in solid state triplet ground states irrespective of the lack of planarity and distinct symmetry. Consequently, the current theories for the prediction of ground-state multiplicities in nondisjoint AH are validated, regardless of these geometrical features.

Finally, the results obtained with the biradical **3** open the possibility of obtaining molecules such as polymer **1** with a very large spin multiplicity and for which a high stability is expected.

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Registry No. **3**, 127316-84-1; **4**, 131380-97-7; **5**, 2136-96-1; **6**, 131380-98-8; $CHCl_3$, 67-66-3; C_6HCl_5, 608-93-5; 1,2,3,5-tetrachlorobenzene, 634-90-2.

Activation of α-Bromo Ketones by Complexation with Hard and Soft Lewis Acids. A Combined X-ray and NMR Study[1]

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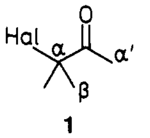
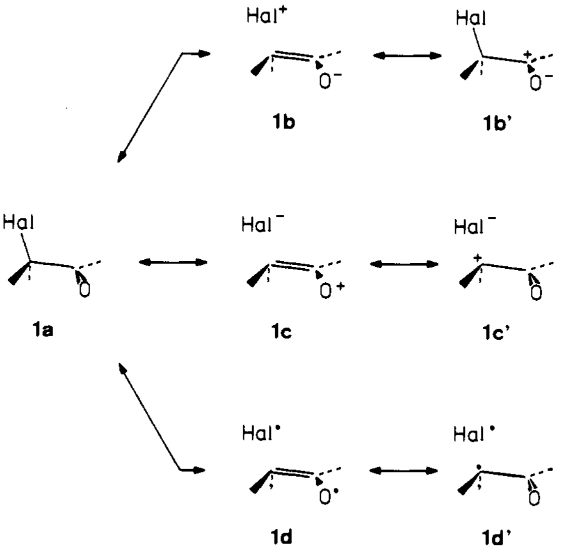
Abstract: α-Halo ketones have two heteroatoms with lone pairs where a Lewis acid can be bound, depending on the softness or hardness of the Lewis acid (HSAB principle). The crystal structures of the complexes **2**·$SbCl_5$, **3**·$SbCl_5$, **8**·$AgSbF_6$, and $(\mathbf{2})_2$·$AgSbF_6$ have been determined in order to analyze the structural and electronic changes in the bromo ketone molecules upon complexation and the different binding properties of a hard ($SbCl_5$) and a soft Lewis acid (Ag^+). The monodentate Lewis acid $SbCl_5$ binds to the oxygen atom, whereas the silver ion is coordinated to the O and the Br atom of a bromo ketone in a chelate-like manner and to the π-systems of phenyl rings. ^1H and ^{13}C NMR measurements of the complexes and of the pure bromo ketones in solution support and complete the results of the X-ray structure determinations: $SbCl_5$ activates the C=O bond by raising the contribution of the C^+—O^- resonance formula, whereas Ag^+ activates preferentially the C—Br bond by raising the contribution of the C^+Br^- resonance formula. The observations are in agreement with reactivity data from the literature.

α-Halo ketones **1** react with a wide variety of reagents[2,3] and are thus an important class of organic compounds. Nucleophiles can not only attack **1** at the carbonyl-C atom (nucleophilic addition), at the halogen (Hal)-substituted α-C atom (nucleophilic substitution), or even at the halogen atom but also deprotonate the α-, α′-, or the β-C atom and initialize different subsequent reactions.[3] The neighborhood of two C atoms prone to nucleophilic attack (**1** can be considered as an ambident electrophile) complicates the prediction of the chemical behavior as well as the conformation of **1**,[4] and therefore some of the earliest works about stereochemical effects by Corey et al.[5] deal with the interaction between the C=O and the C—Hal bonds. In terms of the valence bond (VB) theory, resonance structures **1a** and **1b** are often used in order to explain the variation of the properties of the C—Hal bond with the torsion angle Hal—C—C=O[4,5] (see Scheme I).



1

Scheme I



The credibility of the resonance formula **1b**, however, suffers from the positive charge on the halogen atom (although there is no question about the existence of halonium ions[6,7]), but alternative formulas like **1c** and **1c′** are not better because of the neighborhood of a carbocationic center and a carbonyl group (although the

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[1] Contains parts of the diploma theses of A.W. (ETH Zürich, June 1989) and R.H. (ETH Zürich, June 1990).

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